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Electronic and Chemical Properties of $Ce_{0.8}Zr_{0.2}O_2$(111) Surfaces: Photoemission, XANES, Density-Functional, and NO_2 Adsorption Studies

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Introduction: Zirconia-doped ceria ($Ce_{1-x}Zr_xO_2$) is a complex material and an important component of catalysts used in automotive exhaust gas converters [1]. The exact role of pure and Zr-doped ceria to reduce the emission of toxic pollutants such as nitrogen oxides NO_x (NO_2, NO, N_2O) in automobile catalytic converters is not clear [2]. Understanding the details of NO_x chemistry on $Ce_{1-x}Zr_xO_2$ surfaces has both practical and academic interests.

Methods and Materials: CeO_2(111) and $Ce_{1-x}Zr_xO_2$(111) epitaxial thin films (500-700 Å in thickness) were grown onto a Y-stabilized ZrO_2(111) surface by oxygen-plasma-assisted molecular beam epitaxy. The Y-stabilized ZrO_2 substrate (YSZ) contained ~14 atomic % Y. The oxide films were characterized by X-ray diffraction (XRD), reflection high-energy electron diffraction (RHEED), low-energy electron diffraction (LEED) and X-ray photoemission (XPS). For $Ce_{1-x}Zr_xO_2$ mixed-metal oxide systems with compositions of x=0.1, 0.2, and 0.3, the Zr ions substitutionally replace Ce ions within the cubic fluorite lattice structure of CeO_2. Synchrotron-based high-resolution photoemission, XPS, X-ray absorption near-edge spectroscopy (XANES), and first-principle density-functional calculations were used to study the electronic properties. The chemical properties were examined with NO_2 adsorption.

Results: O *K*-edge of XANES and Ce 3d XPS data demonstrate zirconia doping into ceria induces structural and electronic modifications, which are related to the presence of Ce^{3+} cations and oxygen vacancy intrinsic defects. At 300 K, although NO_2 gas dosing on the reduced $Ce_{0.8}Zr_{0.2}O_2$ surface leads to chemisorbed NO_2 as a dominant species without NO_3 formation, depopulation of Ce^{3+} to Ce^{4+} cations was observed. Atomic nitrogen on the reduced surface was detected as a minor product by full decomposition of a fraction of NO_2. By annealing up to 800 K, NO_2 desorbed with atomic N species left on the surface. In the case of low NO_2 exposures at 100 K onto the $Ce_{0.8}Zr_{0.2}O_2$ surface, chemisorbed NO_2 is still the main species. NO_2 starts to desorb at 150 K and remains relatively stable between 200-500 K. On the reduced CeO_{2-x} surface with NO_2 multilayer adsorption at 100 K, the main product of NO_2 reaction is adsorbed NO_3 at annealing up to 200 K, with NO_2 as a major coexisting species on the surface. The nitrate species was desorbed at 500 K. Either thermal annealing at 800 K or NO_2 exposure at 100 K can partially re-oxidize CeO_{2-x}. On the Ne^+ ion bombardment $Zr(Y)O_{2-x}$ surface with minor Zr^{2+} and Zr^0 ion concentrations, chemisorbed NO_2 was the main species for NO_2 exposure at 300 K. In addition, oxidation of Zr^{2+} and Zr^0 to Zr^{4+} states was observed. It appears that the ZrO_2 doping into the CeO_2 oxides considerably modifies NO_2 surface chemistry of ceria catalysts, and the presence and extent of Ce^{3+} ions and oxygen vacancies still play a very important role.

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